Supporting information

Structural evolution during the graphitization of polyacrylonitrile-based carbon fiber as revealed by small-angle X-ray scattering

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Supporting materials that may be of use or interest to the readers for the paper are shown as follows:

S1. The X-ray diffractograms

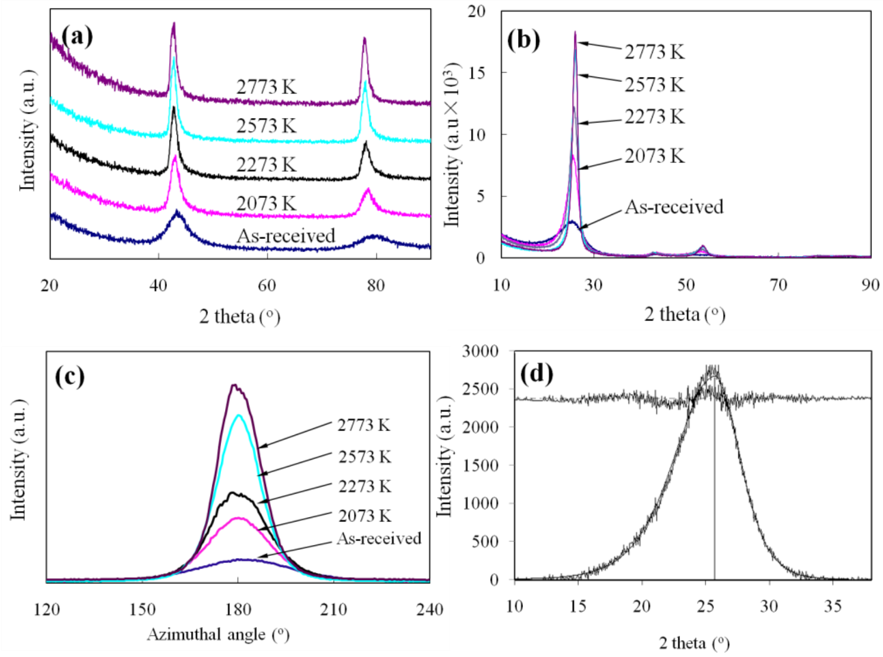

Figure S1 X-ray diffractograms of the (a) meridianal scan, (b) equatorial scan and (c) azimuthal scan at the fixed Bragg position of 002 reflection. (d) The fitting of 002 peak for as-received sample by MDI Jade 5.0.

The XRD diagrams for carbon fibers are shown in Fig. S1. Very broad peaks for 002 (Fig. S1(b)) and 100/101 reflections (Fig. S1(a)) were observed for as-received sample, which indicated the sample was poorly crystallized (Li *et al.*, 2007, Qin *et al.*, 2012). These broad peaks changed into sharp ones with the increase of HTT in accordance with the transformation of the amorphous structure.

S2. Guinier plots of the fitting results

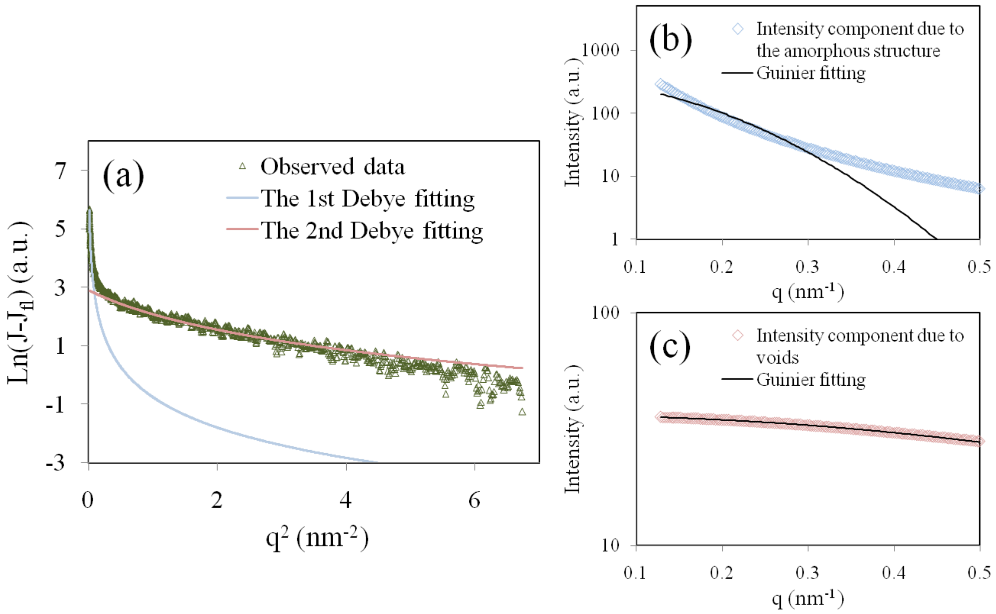

Figure S2 (a) The influence of void and amorphous structure on the total scattering as illustrated by the as-received sample. (b) The fitting for the intensity component due to the amorphous structure (the first Debye fitting). (c) The fitting for the intensity component due to voids (the second Debye fitting).

Fig. S2(a) illustrates the influence of void and amorphous structure on the total scattering intensity. The Guinier fittings for the two intensity components derived from Debye analysis result obvious straight sections in the lower angle area of each Guinier plot (Fig. S2(a) and S2(b)). Integrated the first and second Debye fitting, however, the whole fitting result as well as the observed data show a continuously decreasing ln$J(q)$ with increasing q^2 without obvious straight section. In this condition, the calculated radius of gyration is of some error. By applying 'double Debye' model, the intensity data are separated and the size parameters are thus easy to be determined separately to each kind of scatterers (Fig. S2(a) and S2(b)).

S3. The Debye fitting parameters

Table S1 The Debye fitting parameters for the longitudinal sections of carbon fibers

Sample series	A_1 (a.u.)	A_2 (a.u.)	a_1 (nm)	a_2 (nm)	Reduced Chi-Sqr	Adj. R-Square	$\overline{(\Delta\rho)_1^2}/\overline{(\Delta\rho)_2^2}$ [a]
As-received	4.07×10^3 (101)	18.2 (0.186)	19.3 (0.912)	0.857 (8.52×10^{-3})	1.26	0.9985	0.441
2073 K	1.62×10^4 (614)	253 (3.08)	19.8 (0.638)	1.30 (3.51×10^{-2})	115	0.9997	0.276
2273 K	4.90×10^3 (125)	509 (14.3)	14.1 (0.575)	2.02 (1.51×10^{-2})	61. 6	0.9993	0.197
2573 K	2.45×10^3 (106)	1.34×10^3 (26.4)	10.4 (1.04)	2.43 (2.54×10^{-2})	3.76	0.9999	0.0996
2773 K	---	1.69×10^3 (68.0)	---	3.47 (8.11×10^{-3})	30.6	0.9995	---

[a] $\overline{(\Delta\rho)_1^2}/\overline{(\Delta\rho)_2^2}$, the scattering power contrast of the amorphous vs crystalline carbon against the void vs carbon calculated based on the integral invariant (Guinier & Fournet, 1955). The subscript 1 denotes the first Debye fitting (the scattering originated from the interfibrillar amorphous regions). The subscript 2 denotes the second Debye fitting (the signal from the needle-like microvoids within the crystallites).

The scattering power $\overline{(\Delta\rho)^2}$ can be estimated from the integral invariant as (Guinier & Fournet, 1955):

$$\overline{(\Delta\rho)^2} = \frac{1}{4\pi^2 V I_e}\int_0^\infty qJ(q)dq \qquad (1)$$

where I_e is the intensity scattered by one electron and V the irradiation volume of the sample. An accurate calculation based on the equation needs to know the absolute scattering intensity which is unfortunately not available in the current experimental condition. Nevertheless, we obtained $\overline{(\Delta\rho)_1^2}/\overline{(\Delta\rho)_2^2}$, the scattering power contrast of the amorphous vs crystalline carbon against the void vs carbon from the separated intensity data based on “double Debye” fitting.

Table S2 The Debye fitting parameters for the transverse sections of carbon fibers

Sample series	A_1 (a.u.)	A_2 (a.u.)	a_1 (nm)	a_2 (nm)	Reduced Chi-Sqr	Adj. R-Square	$\overline{(\Delta\rho)_1^2}/\overline{(\Delta\rho)_2^2}$ [a]
As-received	1.19×10^4 (38.2)	261 (7.79)	6.37 (1.99×10^{-2})	0.653 (1.28×10^{-2})	29.7	0.9965	0.481
2073 K	7.22×10^3 (17.5)	617 (5.16)	5.37 (1.49×10^{-2})	0.820 (8.23×10^{-3})	90.7	0.9982	0.273
2273 K	8.16×10^4 (19.3)	1.45×10^3 (14.3)	5.09 (1.65×10^{-2})	1.01 (8.64×10^{-3})	158	0.9974	0.223
2573 K	8.20×10^3 (14.2)	2.64×10^3 (9.33)	4.96 (1.17×10^{-2})	1.23 (5.25×10^{-3})	78.8	0.9997	0.193
2773 K	---	2.93×10^3 (84.3)	---	1.52 (3.16×10^{-2})	827	0.9971	---

[a] $\overline{(\Delta\rho)_1^2}/\overline{(\Delta\rho)_2^2}$, the scattering power contrast of the amorphous vs crystalline carbon against the void vs carbon calculated based on the integral invariant (Guinier & Fournet, 1955).

References

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